

English translation  
of (1)

PTO 98-3129

CY=JP DATE=19960213 KIND=A  
PN=08-38909

OXIDATION CATALYST AND OXIDIZING METHOD USING IT  
[Sanka shokubai oyobi sore wo mochiita sanka hoho]

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UNITED STATES PATENT AND TRADEMARK OFFICE  
Washington, D.C. June 1998

Translated by: FLS, Inc.

PUBLICATION COUNTRY (10) : JP  
DOCUMENT NUMBER (11) : 0838909  
DOCUMENT KIND (12) : A  
(13) :  
PUBLICATION DATE (43) : 19960213  
PUBLICATION DATE (45) :  
APPLICATION NUMBER (21) : 06201434  
APPLICATION DATE (22) : 19940802  
ADDITION TO (61) :  
INTERNATIONAL CLASSIFICATION (51) : B01J 31/06; C07B 33/00;  
C07B 41/00; C07C 27/00;  
C07D 209/48; C07C 47/54;  
C07C 49/403; C07C 49/67;  
C07C 49/786; C07C 51/235;  
C07C 63/06; C07D 311/76;  
//C07B 61/00; C07D 209/48  
DOMESTIC CLASSIFICATION (52) :  
PRIORITY COUNTRY (33) :  
PRIORITY NUMBER (31) :  
PRIORITY DATE (32) :  
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TITLE (54) : OXIDATION CATALYST AND  
OXIDIZING METHOD USING IT  
FOREIGN TITLE [54A] : SANKA SHOKUBAI OYONI SORE  
WO MOCHIITA SANKA HOHO

(54) [Title of the Invention]

Oxidation Catalyst and Oxidizing Method Using It

(57) [Summary]

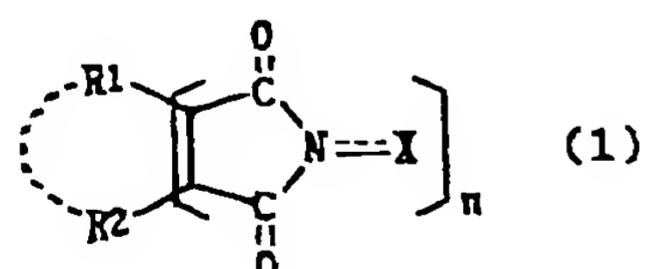
[Purpose]

To obtain the target oxidation compound with which a substrate is oxidized by molecular oxygen with good efficiency under moderate conditions at a high reaction inversion rate and selectivity.

[Constitution]

Oxidation is done by contacting a substrate, such as a hydrocarbon, alcohol, aldehyde and ketone, with molecular oxygen in the presence of ① an oxidation catalyst comprising an imide compound, such as N-hydroxyphthalimide, represented by the general formula (1) and ② a catalyst constituted from a cooxidant, such as the above-mentioned imide compound and a transition metal compound (e.g., an oxide, halide, complex, heteropoly acid salt). If cyclohexane is oxidized, cyclohexanone, cyclohexanol or adipic acid is obtained at a high reaction inversion and selectivity.

[Formula 1]



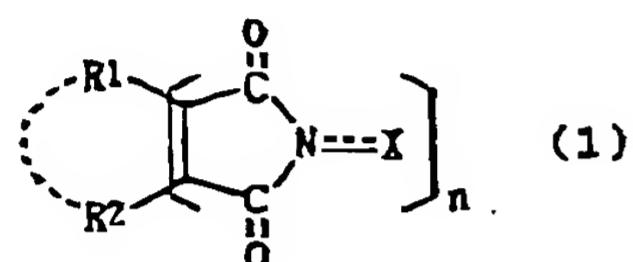
(Where R<sup>1</sup> and R<sup>2</sup> denote substituents, such as hydrogen atoms and halogen atoms; R<sup>1</sup> and R<sup>2</sup> may be bonded together to form a double bond aromatic or non-aromatic 5 to 12-membered ring. X denotes O

or OH, n = 1 to 3.)

[Claims]

[Claim 1]

An oxidation catalyst, which is a catalyst for oxidizing a substrate with molecular oxygen, constituted from an imide compound represented by the general formula (1)



(Where R<sup>1</sup> and R<sup>2</sup> are the same or different and denote hydrogen atoms, halogen atoms, alkyl groups, aryl groups, cycloalkyl groups, hydroxyl groups, alkoxy groups, carboxyl groups, alkoxycarbonyl groups and acyl groups; R<sup>1</sup> and R<sup>2</sup> may be bonded together to form a double bond or an aromatic or nonaromatic ring. X denotes an oxygen atom or hydroxyl group and n denotes an integer from 1 to 3.)

[Claim 2]

The oxidation catalyst of Claim 1 wherein R<sup>1</sup> and R<sup>2</sup> in the imide compound represented by general formula (1) are bonded together to form an aromatic or non-aromatic 5 to 12-membered ring.

[Claim 3]

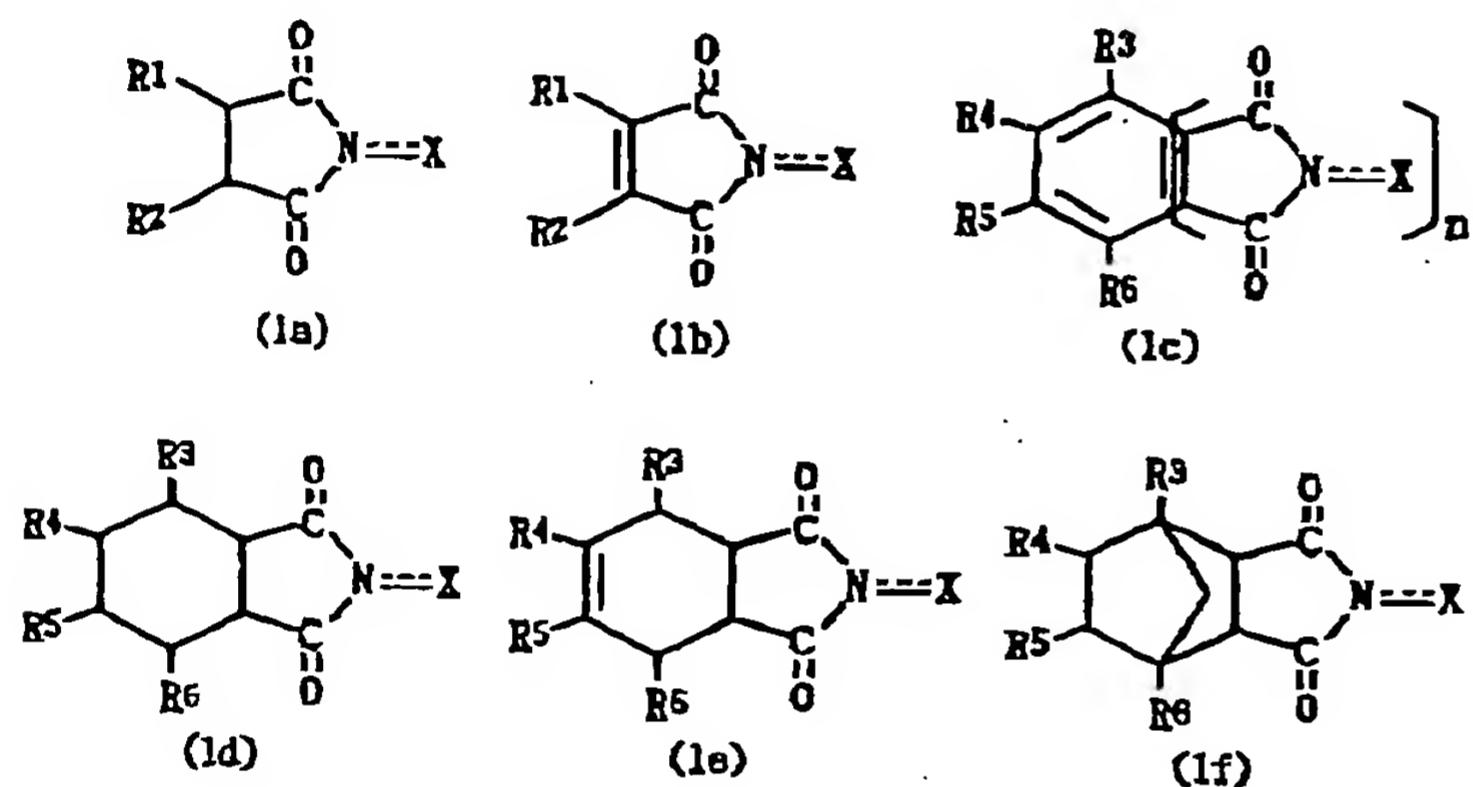
The oxidation catalyst of Claim 1 wherein R<sup>1</sup> and R<sup>2</sup> in the imide compound represented by general formula (1) are bonded together to form a cycloalkane ring that may have a substituent, a cycloalkene ring that may have a substituent, a crosslinked

hydrocarbon ring that may have a substituent, and an aromatic ring that may have a substituent.

[Claim 4]

The oxidation catalyst of Claim 1 wherein the imide compound represented by the general formula (1) is a compound represented by the following general formulas (1a) to (1f).

[Formula 2]



(Where  $R^3$  to  $R^6$  are the same or different and denote hydrogen atoms, alkyl groups, hydroxyl groups, alkoxy groups, carboxyl groups, alkoxycarbonyl groups, acyl groups, nitro groups, cyano groups, amine groups and halogen atoms.  $R^1$ ,  $R^2$  and  $n$  are the same as stated above.)

[Claim 5]

The oxidation catalyst of Claim 1 wherein the imide compound represented by the general formula (1) is at least one kind of compound selected from a group comprising a N-hydroxysuccinic acid imide, N-hydroxymaleic acid imide, N-hydroxyhexahydrophthalic acid imide, N,N'-dihydroxycyclohexane

tetracarboxylic acid imide, N-hydroxyphthalic acid imide, N-hydroxytetrabromophthalic acid imide, N-hydroxytetrachlorophthalic acid imide, N-hydroxy HET acid imide, N-hydroxyhimic acid imide, N-hydroxytrimellitic acid imide, N,N'-dihydroxypyromellitic acid imide and N,N'-dihydroxynaphthalene tetracarboxylic acid imide.

[Claim 6]

The oxidation catalyst of Claim 1 wherein the imide compound represented by the general formula (1) is N-hydroxyphthalimide.

[Claim 7]

The oxidation catalyst of Claim 1 constituted from the imide compound represented by the general formula (1) and a cooxidant.

[Claim 8]

The oxidation catalyst of Claim 7 wherein the cooxidant is a transition metal compound or boron compound.

[Claim 9]

The oxidation catalyst of Claim 7 wherein the cooxidant is at least one kind of compound selected from boric acid, a borate, an oxide containing a group 3, 5, 6, 7, 8, 9, 10 or 11 element of the periodic table, organic salt, halide, complex, and a heteropoly acid or its salt.

[Claim 10]

The oxidation catalyst of Claim 7 wherein the cooxidant is at least one kind of compound selected from a group comprising a compound containing an element selected from a lanthanoid element, V, Mo, W, Fe, Ru, Co, Rh, Ni or Cu, an organic salt,

inorganic salt, halide, complex, and a heteropoly acid or its salt.

[Claim 11]

The oxidation catalyst of Claim 7 wherein the cooxidant is a heteropoly acid salt containing at least one kind of element including V, Mo and W, a transition metal compound containing at least one kind of element including a lanthanoid element, Ru, Co and Cu.

[Claim 12]

The oxidation catalyst of Claim 7 wherein the ratio of the imide compound represented by the general formula (1) to the cooxidant is the imide compound/cooxidant (= 95/5 to 5/95 (mole ratio)).

13

[Claim 13]

An oxidizing method in which the substrate and the molecular oxygen are contacted in the presence of the oxidation catalyst in any of Claims 1 to 12.

[Claim 14]

The oxidizing method of Claim 13 wherein the substrate is a hydrocarbon, alcohol, aldehyde, ketone, amine or heterocyclic compound.

[Claim 15]

The oxidizing method of Claim 14 wherein the hydrocarbon is (1) a compound having a carbon-hydrogen bond at a site adjacent to an unsaturated bond, (2) a nonaromatic cyclic hydrocarbon, (3) a condensation cyclic compound containing a nonaromatic ring and

(4) a crosslinked cyclic hydrocarbon containing a tertiary carbon.

[Claim 16]

The oxidizing method of Claim 14 wherein the alcohol is a primary or secondary alcohol.

[Claim 17]

The oxidizing method of Claim 13 wherein the amount of imide compound represented by the general formula (1) is 0.001 to 1 mole per mole of the substrate.

[Claim 18]

The oxidizing method of Claim 13 wherein the amount of the cooxidant used is 0.001 to 0.7 mole per mole of the substrate.

[Claim 19]

The oxidizing method of Claim 13 wherein the amount of the heteropoly acid or its salt used is 0.1 to 25 weight parts per 100 weight parts substrate.

[Claim 20]

The oxidizing method of Claim 13 wherein 0.01 to 0.5 mole of the imide compound represented by the general formula (1) is used per mole of substrate, and at the same time, (a) 0.005 to 0.5 mole of the cooxidant is used per 100 weight parts substrate or (b) 0.5 to 10 weight parts heteropoly acid or its salt is used per 100 weight parts substrate.

[Claim 21]

The oxidizing method of Claim 13 in which at least one kind of substrate selected from a group including (1) a hydrocarbon

compound having a carbon-hydrogen bond at an allyl site or benzyl site, (2) a cycloalkane that may have a substituent, (3) a condensation cyclic hydrocarbon containing a cycloalkane ring or nonaromatic heterocycle, (4) a crosslinked heterocyclic compound containing a tertiary carbon, (5) a compound having a hydroxymethyl group at a site adjacent to an unsaturated bond, (6) an alicyclic alcohol, (7) an alicyclic alcohol having a tertiary carbon, (8) an aldehyde compound and (9) a ketone is oxidized in the presence of an imide compound in which R<sup>1</sup> and R<sup>2</sup> in the general formula (1) are bonded together to form a cyclohexane ring that may have a substituent, a cyclohexene ring that may have a substituent, a 5-norbornene ring that may have a substituent, or a benzene ring that may have a substituent.

[Claim 22]

The oxidizing method of Claim 21 wherein the reaction is done at a temperature of 0 to 300° under normal or increased pressure.

[Claim 23]

The oxidizing method of Claim 21 wherein the reaction is done by using 0.05 mole to 0.30 mole of the imide compound per mole of the substrate at a temperature of 50 to 200° and a pressure of 1 to 50 atm.

[Claim 24]

The oxidizing method of Claim 23 wherein oxidation is also done by using (a) 0.01 to 0.3 mole of the cooxidant per mole of the substrate or (b) 1 to 5 weight parts heteropoly acid or its

salt per 100 weight parts substrate.

[Claim 25]

An oxidizing method in which a cycloalkane that may have a substituent is oxidized with molecular oxygen in the presence of the oxidation catalyst of Claim 1 or 7, and a cycloalkanone, cycloalkanol or dicarboxylic acid that may have a substituent is formed.

[Claim 26]

The oxidizing method of Claim 25 in which cyclohexane is oxidized with molecular oxygen, and cyclohexanone, cyclohexanol or adipic acid is formed.

[Claim 27]

A method for manufacturing adipic acid in which cyclohexane, cyclohexanone or cyclohexanol is oxidized with molecular oxygen in the presence of the oxidation catalyst of Claim 1 or 7 and adipic acid is generated.

[Detailed Specifications]

[0001] [Field of Industrial Utilization]

The present invention pertains to an oxidation catalyst for manufacturing an alcohol, carbonyl compound, organic acid, and the like, and an oxidizing method using this catalyst.

[0002] [Prior Art]

An oxidation reaction is one of the most basic reactions in organic chemistry industry; hence, a variety of oxidizing methods have been developed. The preferred oxidizing method is a catalytic oxidizing method in which molecular oxygen or air is

utilized directly as an oxidant from the standpoint of natural resources and environment. However, in a catalytic oxidizing method, high temperature and pressure are required for activating the oxygen and it is necessary that the reaction occur under coexistence of a reducing agent, such as an aldehyde, in order that the reaction is done in mild conditions. And so, the inversion rate and selectivity are also still low in a catalytic oxidizing method; hence, it is difficult to manufacture an alcohol, carbonyl compound and organic oxygen with good efficiency by utilizing an oxidation reaction.

[0003]

For example, adipic acid, which is a raw material for nylon 66, is manufactured in a method in which only cyclohexanol or a mixture containing cyclohexanol and cyclohexane (KA oil) is oxidized with nitric acid. And the aforementioned KA oil is manufactured in (1) an oxidizing method in which molecular oxygen is directly and catalytically contacted with cyclohexane as the oxidant, (2) a method for catalytically hydrogenating a phenol, (3) a method in which benzene is partially hydrogenated in cyclohexane by using a ruthenium catalyst and then hydrolyzed. In the aforementioned catalytic oxidizing method (1), a cobalt catalyst, boric acid catalyst, and the like are developed as effective catalyst systems. However, in this catalytic oxidizing method, the selectivity is low and numerous compounds are by products, centering around low molecular weight by products. Therefore, by controlling the reaction inversion rate to about 5

to 10 %, for example, a high selectivity of at least 90 % is maintained.

[0004]

14

In the other oxidizing method (2), and in particular, the other method (3) in which a KA oil is formed from benzene, the production efficiency for KA oil in the rate limiting step in the manufacturing process for adipic acid may be higher than that of the aforementioned catalytic oxidizing method (1). However, manufacturing costs for adipic acid may not be reduced from the standpoint of the number of manufacturing processes.

[0005]

Furthermore, expensive exhaust gas treatment facilities are necessary in all of the aforementioned methods in order to treat the  $N_2O$  and  $NO_x$  formed by nitric acid oxidation. Although methods for manufacturing adipic acid in a butadiene-oxidizing carbonylation method, CO insertion method, or the like has been investigated from these standpoints, these investigations still have not lead to technical industrialization.

[0006]

In particular, a method in which a stable phenoxy nitroxide that is soluble in an organic solvent is also known as an oxidizing method. In an oxidation reaction with a nitroxide, the universality of a substrate under mild conditions is also widespread, but it is particularly distinctive from the standpoint that oxidation of a primary hydroxyl group is performed selectively. Meanwhile, a radical reaction mechanism

via a nitrosonium intermediate (nitrosyl) from a nitroxide (nitroso compound) has been suggested regarding the mechanism of an oxidation reaction in which a nitroxide is used. In addition, (1) a method in which a radical is generated by electrolysis, (2) a method in which a radical generator is added; (3) a method in which a halogen is blown in, (4) a method in which an equivalent weight copper chloride-oxygen system is used, and the like have been proposed as methods in which the nitrosonium intermediate is formed. However, the electrolysis method (1) is difficult from the standpoint of the manufacturing scale. The method (2) in which a radical generator is used is difficult from the standpoint of recycling the catalyst system. In addition, it is necessary to treat the hydrohalide formed in the method (3) in which a halogen is introduced, and at the same time, a problem occurs because the equipment becomes corroded. In addition, in the method (4) in which a copper chloride-oxygen system is used, a large amount of copper chloride is required, which is an economical disadvantage, and at the same time, supplying oxygen is essential for reoxidizing the copper chloride.

[0007]

Meanwhile, a nitroxide also has been investigated. a nitroxide compound having a piperidine skeleton, such as 2,2,6,6-tetramethyl piperidine-1-oxyl (TEMPO), 4-methoxy-2,2,6,6-tetramethyl-1-oxopiperidium chloride and 2,2,6,6-tetramethyl piperidine, and high catalyst activity has been reported (J. Organic Synthesis Chemistry Society, 51, 10 (1993)).

[0008]

Thus, cooxidants have been investigated instead of chlorine or copper chloride for catalysts comprising a nitroxide compound having a piperidine skeleton. For example, TEMPO-*m*-chloro perbenzoic acid (*J. Org. Chem.*, **40**, 1998 (1975)), NaOCl (*J. Org. Chem.*, **52**, 2559 (1987)), NaBrO<sub>2</sub> (*J. Org. Chem.*, **55**, 426 (1990)), tetraammonium bromide (*Bull. Chem. Soc. Jpn.*, **64**, 796 (1991)), and the like have been proposed. These catalyst systems exhibit relatively satisfactory results and are useful oxidation means. However, various limits have been incurred from the standpoint of regeneration of the cooxidant, control of the reaction conditions, etc. Thus, it is difficult to do oxidization at a high inversion rate and selectivity and good efficiency in a simple, universal method.

[0009] [Problems Which the Invention Intends to Solve]

Consequently, an objective of the present invention is to offer an oxidation catalyst capable of oxidizing a substrate using molecular oxygen with good efficiency under moderate conditions in the absence of a special reducing agent, and an oxidizing method using it.

[0010]

Another objective of the present invention is to offer an oxidation catalyst capable of forming the target oxidation compound with molecular oxygen at a high reaction inversion rate and selectivity, and an oxidizing method.

[0011]

Yet another objective of the present invention is to offer an oxidation catalyst capable of manufacturing an alcohol, carbonyl compound, aldehyde compound and organic carboxylic acid under moderate conditions at a high inversion rate and selectivity without particularly requiring an exhaust gas treatment, and an oxidizing method.

[0012]

Still another objective of the present invention is to offer an oxidation catalyst capable of effectively manufacturing KA oil and adipic acid with molecular oxygen in moderate conditions at a high inversion rate and selectivity, and an oxidizing method.

[0013] [Means Used to Solve the Problems]

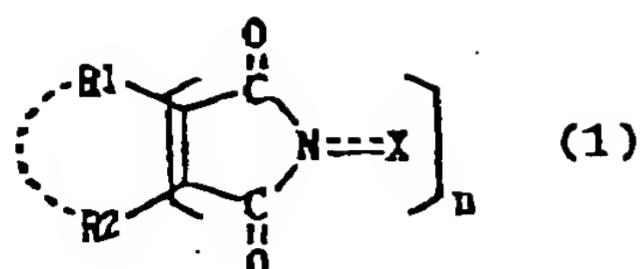
As a result of painstaking investigations in order to achieve the aforementioned objectives, the inventors of the present invention discovered that a substrate to be oxidized, such as an alcohol or hydrocarbon, may be oxidized with good efficiency at a high inversion rate and selectivity without adding a special reducing agent if an N-hydroxyphthalimide compound is used as the catalyst, and they achieved the present invention.

[0014]

That is, the oxidation catalyst of the present invention is an oxidation catalyst, which is a catalyst for oxidizing a substrate with molecular oxygen, and it is constituted from an imide compound represented by the general formula (1).

[0015]

[Formula 3]



(Where  $R^1$  and  $R^2$  are the same or different and denote hydrogen atoms, halogen atoms, alkyl groups, aryl groups, cycloalkyl groups, hydroxyl groups, alkoxy groups, carboxyl groups, alkoxy carbonyl groups and acyl groups;  $R^1$  and  $R^2$  may be bonded together to form a double bond or an aromatic or nonaromatic ring.  $X$  denotes an oxygen atom or hydroxyl group and  $n$  denotes an integer from 1 to 3.)

In the above-mentioned general formula (1),  $R^1$  and  $R^2$  are bonded together to form an aromatic or nonaromatic 5 to 12-membered ring, such as a cycloalkane ring, cycloalkene ring, crosslinked hydrocarbon ring and aromatic ring. Moreover, 15 N-hydroxyphthalimide is utilized as a mediator for electrooxidation, but it is known that it exhibits high activity in oxidation of a substrate with molecular oxygen.

[0016]

The oxidation catalyst may be constituted from the imide compound represented by the general formula (1) and a cooxidant. The cooxidant is constituted from a transition metal compound (e.g., oxide, organic acid salt, inorganic acid salt, halide, complex, heteropoly acid or its salt, etc.), a boron compound,

etc.

[0017]

In the method of the present invention, oxidation is done by contacting the substrate and molecular oxygen in the presence of the aforementioned oxidation catalyst. Various compounds, such as hydrocarbons, alcohols, aldehydes, ketones, amines, heterocyclic compounds, and the like are included as the substrate.

[0018]

The oxidizing method of the present invention may be performed at a temperature of 0 to 300° under normal or increased pressure. The reaction progresses smoothly even in moderate conditions. Thus, if a cycloalkane that may have a substituent is oxidized with molecular oxygen, a cycloalkanone, cycloalkanol or dicarboxylic acid that may have a substituent may be formed. In addition, if cyclohexane is used as the substrate for instance, cyclohexanone, cyclohexanol or adipic acid may be formed at a high inversion rate and selectivity even in moderate conditions.

[0019]

The present invention is explained in detail next.

[0020]

Iodine, bromine, chlorine and fluorine are included as halogen atoms from among the substituents R<sup>1</sup> and R<sup>2</sup> in the compound represented by the aforementioned general formula (1). A straight or branched chain alkyl group with about 1 to 10

carbons, such as a methyl, ethyl, propyl, isopropyl, butyl, isobutyl, sec-butyl, t-butyl, pentyl, hexyl, heptyl, octyl, decyl group, or the like, is included as the alkyl group. A lower alkyl group with about 1 to 6 carbons, and in particular, about 1 to 4 carbons is cited as an example of the preferred alkyl group.

[0021]

A phenyl group, naphthyl group, and the like are included as the aryl group, and a cyclopentyl, cyclohexyl, cyclooctyl group, and the like are included as the cycloalkyl group. A lower alkoxy group with about 1 to 10, and preferably, about 1 to 6, and in particular, about 1 to 4 carbons, such as a methoxy, ethoxy, propoxy, isopropoxy, butoxy, isobutoxy, t-butoxy, pentyloxy or hexyloxy group, is included as the alkoxy group.

[0022]

An alkoxy carbonyl group with about 1 to 10 carbons in the alkoxy part, such as a methoxycarbonyl, ethoxycarbonyl, propoxycarbonyl, isopropoxycarbonyl, butoxycarbonyl, isobutoxycarbonyl, t-butoxycarbonyl, bentyloxycarbonyl and hexyloxycarbonyl group, is included as the alkoxy carbonyl group. A lower alkoxy carbonyl group with about 1 to 6, and in particular, about 1 to 4 carbons in the alkoxy part is included as the preferred alkoxy carbonyl group.

[0023]

An acyl group with about 1 to 6 carbons, such as a formyl, acetyl, propionyl, butyryl, isobutyryl, valeryl, isovaleryl and pivaloyl group, may be used as an example of the acyl group.

[0024]

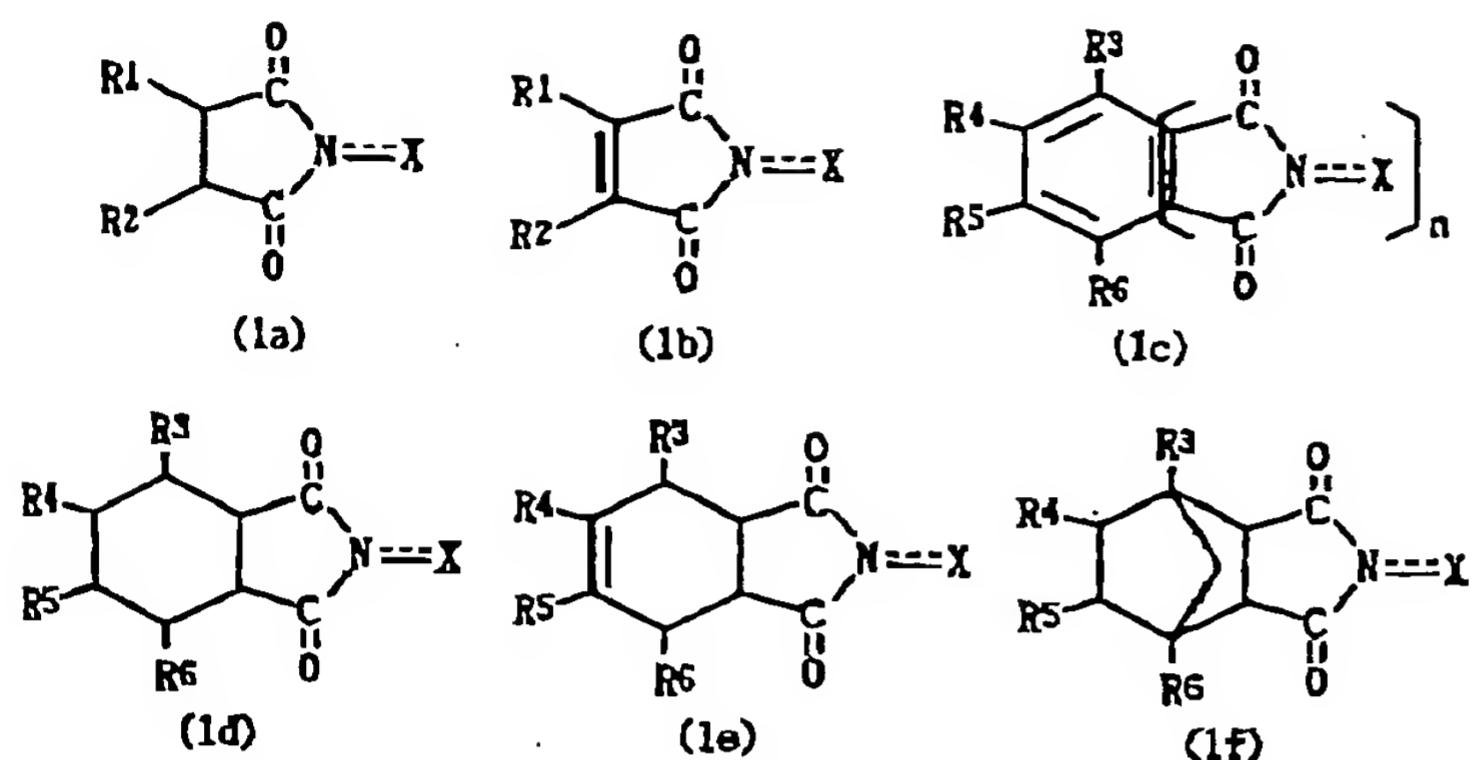
The aforementioned substituents  $R^1$  and  $R^2$  may be the same or different. In addition,  $R^1$  and  $R^2$  in the aforementioned general formula (1) may be bonded together to form a double bond or an aromatic or nonaromatic ring. The preferred aromatic or nonaromatic ring is approximately a 5 to 12-membered, and in particular, approximately a 6 to 10-membered ring. It may be a heterocycle or condensation heterocycle, but it often happens that it is a hydrocarbon ring. A nonaromatic crosslinked ring (a cycloalkane ring that may have a substituent, such as a cyclohexane ring, a cycloalkene ring that may have a substituent, such as a cyclohexene ring, etc.), a nonaromatic crosslinked ring (a crosslinked hydrocarbon that may have a substituent, such as a 5-norbornene ring, etc.) and an aromatic ring that may have a substituent, such as a benzene ring and a naphthalene ring, are included as this kind of ring. It often happens that the aforementioned ring is constituted from an aromatic ring.

[0025]

Compounds represented by the following formulas are included as the preferred imide compounds.

[0026]

[Formula 4]



(Where R<sup>3</sup> to R<sup>6</sup> are the same or different and denote hydrogen atoms, alkyl groups, hydroxyl groups, alkoxy groups, carboxyl groups, alkoxy carbonyl groups, acyl groups, nitro groups, cyano groups, amine groups and halogen atoms. R<sup>1</sup>, R<sup>2</sup> and n are the same as stated above.)

The same alkyl group as the aforementioned exemplified alkyl group, and in particular, an alkyl group with about 1 to 6 carbons is included as the alkyl group. The same alkoxy group as stated above, and in particular, a lower alkoxy group is included as the alkoxy group. The same alkoxy carbonyl group as stated above, and in particular, a lower alkoxy carbonyl group with about 1 to 4 carbons in the alkoxy part is included as the alkoxy carbonyl group. In addition, the same acyl group as stated above, and in particular, an acyl group with about 1 to 6 carbons may be exemplified for the acyl group. A fluorine, chlorine and bromine atom may be exemplified for the halogen atom. It often

happens that the substituents  $R^3$  to  $R^6$  are hydrogen atoms, lower alkyl groups with about 1 to 4 carbons, carboxylic groups, nitro groups and halogen atoms.

[0027]

X in the aforementioned general formula (1) denotes an oxygen atom or hydroxyl group; n is normally about 1 to 3, and preferably, 1 or 2. One or at least two kinds of compounds may be used for the compound represented by the general formula (1) in the oxidation reaction.

[0028]

A saturated or unsaturated aliphatic dicarboxylic acid anhydride, such succinic acid anhydride and maleic acid anhydride; a saturated or unsaturated nonaromatic cyclic polyvalent carboxylic acid anhydride (an alicyclic polyvalent carboxylic acid anhydride), such as tetrahydrophthalic acid anhydride, a hexahydrophthalic acid anhydride (1,2-cyclohexane dicarboxylic acid anhydride), 1,2,3,4-cyclohexane tetracarboxylic acid 1,2-anhydride; a crosslinked cyclic polyvalent carboxylic acid anhydride (alicyclic polyvalent carboxylic acid anhydride), such as HET acid anhydride and himic acid anhydride; and an aromatic polyvalent carboxylic acid anhydride, such as phthalic acid anhydride, tetrabromophthalic acid anhydride, tetrachlorophthalic acid anhydride, nitrophthalic acid anhydride, trimellitic acid anhydride, methylcyclohexene tricarboxylic acid anhydride, pyromellitic acid anhydride, mellitic acid anhydride and 1,8; 4,5-naphthalene tetracarboxylic acid dianhydride, are

included as the acid anhydride corresponding to the imide compound represented by the aforementioned general formula (1).

[0029]

N-hydroxysuccinic acid imide, N-hydroxymaleic acid imide, N-hydroxyhexahydrophthalic acid imide, N,N'-dihydroxycyclohexane tetracarboxylic acid imide, N-hydroxyphthalic acid imide, N-hydroxytetrachlorophthalic acid imide, N-hydroxy HET acid imide, N-himic acid imide, N-hydroxytrimellitic acid imide, N,N'-dihydroxypyromellitic acid imide, N,N'-dihydroxynaphthalene tetracarboxylic acid imide, and the like are cited as examples of preferred imide compounds. Alicyclic polyvalent carboxylic acid imide, and among these, N-hydroxyimide compounds derived from aromatic polyvalent carboxylic acid imides, such as N-hydroxyphthalic acid imide, and the like are included as especially preferred compounds.

[0030]

The aforementioned imide compound may be prepared by the customary imidization reaction, such as ring opening and imidization, after allowing the corresponding acid anhydride and hydroxylamine ( $\text{NH}_2\text{OH}$ ) to react and the acid anhydride group to undergo ring opening.

[0031]

If this kind of imide compound is used, the oxidation activity may be enhanced even if a cooxidant, such as copper chloride, is jointly used, and the oxidation reaction may be catalytically accelerated even at mild conditions. Thus, the

substrate may be oxidized with good efficiency and high selectivity, and alcohols, ketones, aldehydes or organic carboxylic acids may be formed. Furthermore, if the substrate is oxidized under coexistence of the aforementioned imide compound represented by the general formula (1) and a cooxidant, the inversion rate and/or selectivity may be further improved.

[0032]

A metal compound, such as a transition metal compound, and a compound containing a group 13 element of the periodic table (boron (B), aluminum (Al), etc.), such as a boron compound, is included as the cooxidant for a co-catalyst. One cooxidant may be used or at least two of them may be combined.

[0033]

A group 3 element of the periodic table (e.g., outside of scandium (Sc) and yttrium (Y), lanthanoid elements, such as lanthanum (La), cerium (Ce) and samarium (Sm); and actinoid elements, such as actinoid [should be actinium] (Ac)), a group 4 element (titanium (Ti), zirconium (Zr), hafnium (Hf), etc.), a group 5 element (vanadium (V), niobium (Nb), tantalum (Ta), etc.), a group 6 element (chromium (Cr), molybdenum (Mo), tungsten (W), etc.), a group 7 element (manganese (Mn), etc.), a group 8 element (iron (Fe), ruthenium (Rh), osmium (Os), etc.), a group 9 element (cobalt (Co), rhodium (Rh), iridium (Ir), etc.), a group 10 element (nickel (Ni), palladium (Pd), platinum (Pt), etc.), a group 11 element (copper (Cu), silver (Ag), gold (Au), etc.), and the like are cited as examples of the aforementioned

17

transition metal element.

[0034]

A transition metal element (e.g., a group 3 element of the periodic table, such as a lanthanoid element or actinoid element; a group 5 element, such as V and Nb; a group 6 element, such as Cr, Mo and W; a group 7 element, such as Mn; a group 8 element, such as Fe and Ru; a group 9 element, such as Co and Rh; a group 10 element, such as Ni; a group 11 element, such as Cu), and a group 13 element, such as B, are included as the element constituting the preferred cooxidant. In particular, when combined with the imino [sic.] compound represented by the aforementioned general formula (1), a compound containing a lanthanoid element, such as Ce; a group 5 element, such as V; a group 6 element, such as Mo and W; a group 8 element, such as Fe and Ru; a group 9 element, such as Co and Rh; a group 10 element, such as Ni; and a group 11 element, such as Cu, exhibit high oxidation activity.

[0035]

The cooxidant (co-catalyst) is not especially limited as long as it includes the aforementioned elements and has oxidation ability, and it may be a hydroxide and the like, but it often happens that it is a metal oxide containing the aforementioned elements, an organic acid salt, inorganic acid salt, halide, a coordination compound containing the aforementioned metal elements (a complex), a heteropoly acid or its salt. In addition, a boron hydroxide (e.g., boran, diboran, tetraboran,

pentaboran, decaboran); boric acid (o-boric acid, m-boric acid, tetraboric acid); borate (e.g., nickel borate, magnesium borate, manganese borate); a boron oxide, such as  $B_2O_3$ ; a nitrogen compound, such as borozan [as transliterated], borazene [as transliterated], borazine, boron amide and boron imide; a halide, such as  $BF_3$ ,  $BCl_3$ , and tetrafluoroboric acid salts; a boric acid ester (e.g., methyl borate, phenyl borate), are cited as examples of the boron compound. A boric acid or its salt, such as boron hydroxide and o-boric acid, and especially, boric acid is included as the preferred boron compound. One or at least two of these cooxidants may be used.

[0036]

$Sm_2O_3$ ,  $TiO_2$ ,  $CrO$ ,  $Cr_2O_3$ ,  $MnO$ ,  $MnO_2$ ,  $FeO$ ,  $Fe_2O_3$ ,  $RuO_2$ ,  $RuO_4$ ,  $CoO$ ,  $CoO_2$ ,  $Co_2O_3$ ,  $RhO_2$ ,  $Rh_2O_3$ ,  $Cu_2O_3$ , and the like are included as examples of the metal oxide. Cobalt acetate, cobalt propionate, cobalt naphthenate, cobalt stearate, corresponding Ce salts, Cr salts, Mn salts, Fe salts, Ni salts, Pd salts, Cu salts, and the like are exemplified as the organic acid salt. A nitric acid salt, such as nickel nitrate and copper nitrate, or their corresponding sulfuric acid salts or phosphoric acid salts, and the like are cited as examples of the inorganic acid salt. In addition, a chloride, such as  $SmCl_3$ ,  $FeCl_2$ ,  $FeCl_3$ ,  $RuCl_3$ ,  $CoCl_2$ ,  $RhCl_2$ ,  $NiCl_2$ ,  $PdCl_2$ ,  $PtCl_2$ ,  $CuCl$  and  $CuCl_2$ , their corresponding bromides, and the like may be exemplified as the halide.

[0037]

An alkoxy group, such as an OH (hydroxo), methoxy, ethoxy, propoxy and butoxy group; an acyl group, such as an acetyl and propionyl group; an alkoxy carbonyl group, such as a methoxycarbonyl (acetato) and ethoxycarbonyl group; acetyl acetate; a cyclopentadienyl group, a halogen atom, such as chlorine and bromine; CO; CN; an oxygen atom, H<sub>2</sub>O (aquo), a phosphine (e.g., a triarylphosphine, such as triphenylphosphine), a nitrogen-containing compound, such as NH<sub>3</sub> (ammine), NO, NO<sub>2</sub> (nitro), NO<sub>3</sub> (nitrite), ethylene diamine, diethylene triamine, pyridine and phenanthroline, and the like are cited as the ligand constituting the complex. One or at least two kinds of the same kind or various kinds of ligands may be coordinated in the complex or complex salt.

[0038]

A complex containing a transition metal element (e.g., a group 3 element of the periodic table to which a lanthanoid elements or actinoid element, such as Ce, belongs; a group 8 element of the periodic table, such as Fe and Ru; a group 9 element of the periodic table, such as Co and Rh; a group 10 element of the periodic table, such as Ni, Pd and Pt; a group 11 element of the periodic table, such as Cu) is included as the preferred complex. In addition, it often happens that the ligand is e.g., an OH, alkoxy group, acyl group, alkoxy carbonyl group, acetylacetone, halogen atom, CO, CN, H<sub>2</sub>O (aquo), phosphorus compound, such as triphenylphosphine, and nitrogen-containing

compound including  $\text{NH}_3$ ,  $\text{NO}_2$  and  $\text{NO}_3$ . The aforementioned transition metal compound and ligand may constitute a complex by suitably combining them. For example, it may be cerium acetyl acetonate, cobalt acetyl acetonate, ruthenium acetyl acetonate or copper acetyl acetonate.

[0039]

It often happens that the polyacid forming the heteropoly acid is at least one kind of compound containing a group 5 or 6 element of the periodic table, such as V (vanadic acid), Mo (molybdenic acid), and W (tungstenic acid). The central atom is not especially limited. For example, it may be Cu, Be, B, Al, Si, Ge, Sn, Ti, Th, N, P, As, Sb, V, Nb, Ta, Cr, Mo, W, S, Se, Te, Mn, I, Fe, Co, Ni, Rh, Os, Ir, Pt or Cu. A cobalt molybdenic acid salt, cobalt tungstenic acid salt, molybden tungstenic acid salt, vanadium molybdenic acid salt, vanadomolybdophosphate, and the like are cited as specific examples for the heteropoly acid.

[0040]

It often happens that a heteropoly acid salt that contains at least one kind of element including V, Mo and W (e.g., a vanadium-molybdenum heteropoly acid or its salt), a transition metal compound (e.g., a lanthanoid element, and a transition compound that contains at least one kind of element including Ru, Co and Cu) are used for the cooxidant.

[0041]

Moreover, it is predicted that the heteropoly acid in the oxidation catalyst participates in a hydrogen-removing reaction.

It can be predicted that a cobalt compound, boron compound, and the like participates in peroxide decomposition.

[0042]

The catalyst system constituted from the imide compound represented by the general formula (1), or this imide compound and the aforementioned cooxidant may be a homogeneous system or a nonhomogenous system. In addition, the catalyst system may be a solid catalyst in which the catalyst constituent is carried on a carrier. It often happens that a porous carrier, such as activated charcoal, zeolite, silica, silica-alumina and bentonite, is used for the carrier. The amount of the catalyst constituent carried in the solid catalyst is generally about 0.1 to 50 weight parts, preferably, 0.5 to 30 weight parts, and more preferably, 1 to 20 weight parts of the imide compound represented by the general formula (1) per 100 weight parts carrier. In addition, the amount of the cooxidant carried per 100 weight parts carrier is about 0.1 to 30 weight parts, preferably, 0.5 to 25 weight parts, and more preferably, 1 to 20 weight parts.

[0043]

The amount of the imide compound represented by the aforementioned general formula (1) may be selected in a wide range, such as about 0.001 mole (0.1 mole %) to 1 mole (100 mole %), preferably, 0.01 mole (1 mole %) to 0.5 mole (50 mole %), and more preferably, 0.05 mole (1 mole %) to 0.30 mole (30 mole %) per mole of the substrate to be oxidized. It is often happens

that it is about 0.05 mole (5 mole %) to 0.25 mole (25 mole %).

[0044]

In addition, the amount of the co-catalyst (cooxidant) used may be suitably selected in a range that does not reduce the reactivity or selectivity. For example, it is about 0.001 mole (0.1 mole %) to 0.7 mole (70 mole %), preferably, 0.005 to 0.5 mole, and more preferably, 0.01 to 0.3 mole per mole of the substrate to be oxidized. It often happens that it is about 0.005 to 0.1 mole.

[0045]

Moreover, the ratio of the cooxidant to the imide compound represented by the general formula (1) may be selected in a range in which the reaction rate or selectivity are not compromised. For example, the imide compound/cooxidant [ratio] equals about 95/5 to 5/95 (mole ratio), preferably, 90/10 to 20/80 (mole ratio), and more preferably, 85/10 to 50/50 (mole ratio).

[0046]

When a heteropoly acid or its salt is used as the cooxidant, it is about 0.1 to 25 weight parts, preferably, 0.5 to 10 weight parts, and more preferably, 1 to 5 weight parts.

[0047]

If this kind of oxidation catalyst is utilized, the substrate may be oxidized with high efficiency even if it has been extremely difficult to be oxidized in the past. For example, if the inversion rate in the oxidation reaction for a hydrocarbon, such as cyclohexane, was 10 % or higher in the past,

it was a suitable, outstanding oxidizing method, and favorable results were obtained only with a specific substrate, such as diphenyl methane. Meanwhile, in the present invention, an oxidation compound, such as a corresponding carbonyl compound or alcohol, may be achieved at a high yield, such as about 20 to 60 % or higher, merely by stirring the a catalytic amount of the aforementioned compound with a saturated hydrocarbon (e.g., cyclohexane), which is the substrate. Thus, the method of the present invention is effective from the standpoint of introducing a hydroxyl group, carbonyl group, formyl group or carboxyl group into the substrate.

[0048]

In the oxidizing method of the present invention, the substrate is oxidized by contacting it with molecular oxygen in the presence of the aforementioned catalyst. In addition to hydrocarbons, alcohols, aldehydes, ketones, amines and heterocyclic compounds, various compounds like thiols, such as ethane thiol and phenyl methane thiol; sulfides, like diethyl sulfide, methyl propyl sulfide and diphenyl sulfide; amides, such as formamide and acetamide, and the like are cited as examples of the aforementioned substrate.

[0049]

Saturated or unsaturated hydrocarbons, alcohols, aldehydes, amines, heterocyclic compounds, and the like are included as preferred substrates. In addition, a corresponding aldehyde (formyl) compound, ketone compound or organic acid is formed by

oxidation of an alcohol, and the corresponding organic acid is formed by oxidation of the aldehyde compound. Furthermore, a ketone is cleaved by oxidation and the corresponding aldehyde (formyl) compound and organic acid are formed.

[0050]

Saturated or unsaturated hydrocarbons oxidizable by molecular oxygen, such as straight chain and branched aliphatic hydrocarbons (e.g., higher hydrocarbons, and preferably, branched linear saturated hydrocarbons, such as isobutane; branched unsaturated hydrocarbons, such as 2-butene, isobutene, butadiene and isoprene, etc.), alicyclic hydrocarbons, such as cyclobutane, cyclopentane, cyclohexane, cycloheptane, cyclooctane, methylcyclohexane, ethylcyclohexane, dimethylcyclohexane, chlorocyclohexane, methoxycyclohexane, cyclohexene, cyclooctene, cyclopentadiene, cycloocdaene [as transliterated or may be cyclooctadiene] and crosslinked cyclic hydrocarbons (e.g., dicyclopentadiene, adamantane, limonene, terpinene and  $\alpha$ -pinene); condensation cyclic hydrocarbons, such as acenaphthene, indene, fluorene, tetralin and complete or partially hydrogenated condensation cyclic hydrocarbons; aromatic hydrocarbons, such as diphenyl methane, triphenyl methane, dibenzyl and stilbene, and the like are included as hydrocarbons.

[0051]

19

(1) Compounds having a carbon-hydrogen bond at a site adjacent to an unsaturated bond (e.g., compounds having a carbon-hydrogen bond at an allyl or benzyl site), (2) nonaromatic cyclic

hydrocarbons (e.g., a cycloalkane, such as cyclohexane and methyl cyclohexane; a cycloalkene, such as cyclohexene), (3) compounds containing a nonaromatic ring (e.g., a cycloalkane ring or heterocycle), (4) crosslinked cyclic hydrocarbons containing a tertiary carbon (methine carbon), and the like are included as preferred hydrocarbons.

[0052]

Saturated aliphatic monohydric alcohols, such as methanol, ethanol, 1-propanol, isopropanol, 1-butanol, isobutanol, 1-pentanol, 2-pentanol, neopentanol, 1-hexanol, 1-octanol, 1-decanol and higher alcohols (e.g., 1-dodecanol, myristyl alcohol, 1-hexadecanol, etc.); unsaturated aliphatic monohydric alcohols, such as ally alcohol, crotyl alcohol, propargyl alcohol, geraniol and citronellol; aliphatic polyhydric alcohols, such as ethylene glycol, propylene glycol, trimethylene glycol, 1,2-butane diol, 1,3-butane diol, 1,4-butane diol, hexane diol, neopentyl, pinacol and glycerine; alicyclic monohydric alcohols, such as cyclobutanol, cyclopentanol, cyclohexanol, methyl hexanol, cyclohexene-1-ol, 4-hydroxy-1-cyclohexane carboxylic acid, cycloheptanol, cyclooctanol, borneol and menthol; alicyclic polyhydric alcohols, such as 1,2-cyclohexane diol and 1,4-cyclohexane diol; aromatic alcohols, such as benzyl alcohol, salicyl alcohol, benzhydrol and phenetyl alcohol, and the like are cited as examples of alcohols.

[0053]

a primary or secondary alcohol is preferred from among these alcohols and it may be either an aliphatic alcohol, alicyclic alcohol or aromatic alcohol. Moreover, the oxidizing method of the present invention is distinctive from the standpoint that the oxidation reaction proceeds preferentially in a primary alcohol.

[0054]

(1) Compounds having a hydroxymethyl group at a site adjacent to an unsaturated bond (e.g., unsaturated or aromatic alcohols, such as allyl alcohol, benzyl alcohol and benzhydrol), (2) alicyclic alcohols (e.g., cycloalkanols, such as cyclohexanol and methyl cyclohexanol), (3) alicyclic alcohols having a tertiary carbon (methine carbon) (e.g., borneol, etc.), and the like are included as preferred alcohols.

[0055]

Saturated aliphatic aldehydes, (e.g., formaldehyde, acetaldehyde, propionaldehyde, butylaldehyde, hexanal, higher aldehydes (octaaldehyde, nonaldehyde, etc.); unsaturated aliphatic aldehydes (e.g., acrolein, etc.), glyoxal, methyl glyoxal, aliphatic polyaldehydes (e.g., malonaldehyde, succinaldehyde, glytalaldehyde, adipinaldehyde [as transliterated], pimelinaldehyde [as transliterated], suberinaldehyde [as transliterated], sebacinaldehyde), aliphatic aldehydes, such as aminoacetaldehyde; aromatic aldehydes, such as benzaldehyde, oxybenzaldehyde, nitrobenzaldehyde, oxybenzaldehyde, nitrobenzaldehyde, aminobenzaldehyde,

cinnamaldehyde, alicylaldehyde, anisaldehyde, 1-naphthyl acetaldehyde, vanillin (vanylaldehyde [as transliterated]), phthalaldehyde, isophthalaldehyde and terephthalaldehyde; alicyclic aldehydes, such as formyl cyclohexane, citronellal and citral; heterocyclic aldehydes, such as nicotinaldehyde, and the like are cited as examples of aldehydes.

[0056]

Aliphatic ketones, such as acetone, methyl ethyl ketone, diethyl ketone, dipropyl ketone, methyl propyl ketone, methyl butyl ketone and pinacolone; alicyclic ketones (cyclic ketones), such as cyclopentanone, cyclohexanone, cyclooctanone, 2-methyl cyclohexanone, 2-ethyl cyclohexanone, 2,6-dimethyl cyclohexanone, 4-chlorocyclohexanone, 4-methoxycyclohexanone, menthone and camphor; aromatic ketones, such as acetophenone, propionphenone, benzophenone, deoxybenzoin and 1-naphthalenone; heterocyclic ketones, such as indene-1-on, 1,2,3-indanthrone, fluorene-9-on and 4-pyranone, are cited as ketones.

[0057]

Primary and secondary amines like aliphatic amines, such as methyl amine, ethyl amine, propyl amine, butyl amine, dimethyl amine, diethyl amine, dibutyl amine, ethylene diamine, 1,4-butane diamine, hydroxyl amine and ethanolamine; alicyclic amines, such as cyclopentyl amine and cyclohexyl amine; aromatic amines, such as benzyl amine and toluidine, and the like are exemplified as amines. Amines are oxidized into corresponding Schiff bases, oximes, and the like due to oxidation.

[0058]

Condensation cyclic hydrocarbons containing a nonaromatic heterocyclic compound or nonaromatic heterocycle, such as pyran, pyrazoline, piperidine, piperazine, indoline, isoindoline, chromene, xanthene, chroman, isochroman, and the like are exemplified as heterocyclic compounds.

[0059]

The molecular oxygen utilized in oxidation of the substrate is not especially limited and pure oxygen may be used, or oxygen diluted with an inert gas, such as nitrogen, helium, argon, carbon dioxide, and the like may be used. Using air is preferred from the standpoint of economics and the like in addition to processability and safety.

[0060]

110

The amount of molecular oxygen used may be selected according to the type of substrate and target compound; normally, it is about at 0.5 mole or higher (e.g., at least one mole), preferably, 1 to 100 moles, and more preferably, 2 to 50 moles per mole of the substrate compound. It often happens that excess moles of molecular oxygen are used with respect to the substrate.

[0061]

The oxidizing method of the present invention is normally performed in an inert organic solvent during the reaction. Organic acids, such as acetic acid and propionic acid; nitriles, such as acetonitrile, propionitrile and benzonitrile; amides, such as formamide, acetamide, dimethylformamide (DMF) and

dimethylacetamide; alcohols, such as *t*-butanol and *t*-amyl alcohol; aliphatic hydrocarbons, such as hexane and octane; aromatic hydrocarbons, such as benzene and toluene; halogenated hydrocarbons, such as chloroform, dichloromethane, dichloroethane, carbon tetrachloride and chlorobenzene; nitro compounds, such as nitrobenzene, nitromethane and nitroethane; esters, such as ethyl acetate and butyl acetate; ethers, such as dimethyl ether, diethyl ether, diisopropyl ether, dioxane and tetrahydrofuran; solvent mixtures of these compounds, and the like are cited as examples of organic solvents. Moreover, the substrate may be utilized as the reaction solvent by using an excess amount of substrate. It often happens that a nitrile, such as benzonitrile, is used.

[0062]

There is a distinguishing characteristic in the method of the present invention in that the oxidation reaction proceeds smoothly even at relatively moderate conditions. The reaction temperature may be suitably selected according to the type of substrate, etc. For example, it reacts at about 0 to 300°C, preferably, 30 to 250°C, and more preferably, 50 to 200°C. It often happens that it normally reacts at about 70 to 150°C. In addition, the reaction may be performed under normal or increased pressure. When it reacts under increased pressure, it often happens that it is usually about 1 to 100 atm (e.g., 1.5 to 80 atm), preferably, 2 to 70 atm, and more preferably, 5 to 50 atm. The reaction time may be suitably selected according to the

reaction temperature and pressure, for example, from a range of about 30 minutes to 48 hours, preferably, 1 to 36 hours, and more preferably, 2 to 24 hours.

[0063]

Moreover, when the reaction temperature and/or reaction pressure is high, the oxidation reaction rate may be increased, but a carboxylic acid or a peroxide is sometimes a by-product.

[0064]

The method of the present invention is effective from the standpoint of oxidizing various compounds under moderate conditions at a high inversion rate and selectivity, as stated above, and obtaining alcohols, aldehydes, ketones and organic acids. In particular, if a cycloalkane having a substituent is used as the substrate, the corresponding cycloalkanol, cycloalkanone and dicarboxylic acid having a substituent may be obtained at a high yield while suppressing side reaction(s). Thus, if cyclohexane is used as the substrate, cyclohexanol, cyclohexanone and adipic acid are formed. In addition, cyclohexanol and cyclohexanone (KA oil) finally may be converted to adipic acid by oxidation. Consequently, in addition to a method for manufacturing alcohols, aldehydes, ketones and organic acids, the oxidizing method of the present invention is extremely effective from the standpoint of manufacturing adipic acid that serves as a raw material for nylon 66, and the like by contacting at least one constituent including cyclohexane, cyclohexanole and cyclohexanone.

[0065]

The reaction may be performed in the customary method, such as a batch, semibatch and continuous method, in the presence or under circulation of molecular oxygen. After the reaction is completed, the reaction product may be easily separated and purified in the customary method like a separation means, such as filtration, concentration, distillation, extraction, crystallization, recrystallization and column chromatography, and a combination of these means.

[0066] [Merits of the Invention]

With the oxidation catalyst and oxidizing method of the present invention, the oxidation catalyst is constituted from ① an imide compound represented by the general formula (1) and ② this imide compound and a cooxidant; hence, the substrate may be oxidized with molecular oxygen under moderate conditions with good efficiency in the absence of a special reducing agent. In addition, the target oxidation compound may be formed with molecular oxygen at a high reaction inversion rate and selectivity. Furthermore, air may be utilized as molecular oxygen. Thus, alcohols, carbonyl compounds, aldehyde compounds and organic carboxylic acids may be manufactured in a simple operation under moderate conditions at a high inversion rate and selectivity, and particularly without requiring a gas exhaust treatment. It is also useful from an economics and safety standpoint.

[0067]

Furthermore, the aforementioned oxidation catalyst is used in the method of the present invention; hence, at moderate conditions, KA oil and adipic acid may be manufactured effectively from cyclohexane at a high inversion rate and selectivity by using molecular oxygen.

[0068] [Practical Examples]

The present invention is explained in further detail next on the basis of the practical examples, but the present invention is not limited to these practical example whatsoever.

[0069] Practical Example 1

A solution mixture containing 184 weight parts (1 mole) benzhydrol, 16 weight parts (0.1 mole) N-hydroxyphthalimide and 1,000 weight parts benzonitrile was stirred for 5 hours at 100°C under an oxygen atmosphere. Upon investigating the product in the reaction solution by means of gas chromatographic analysis, 140 weight parts benzophenone (76 % yield) were formed.

[0070] Practical Example 2

A solution mixture containing 184 weight parts (1 mole) benzhydrol, 16 weight parts (0.1 mole) N-hydroxyphthalimide, 7 weight parts vanadomolybdophosphosphate ( $NPV_6Mo_6$ ) and 1,000 weight parts benzonitrile was stirred for 5 hours at 100°C under an oxygen atmosphere. Upon investigating the product in this reaction solution by means of gas chromatographic analysis, 180 weight parts benzophenone (99 % yield) were formed.

/11

[0071] Practical Example 3

A solution mixture containing 184 weight parts (1 mole) benzhydrol, 16 weight parts (0.1 mole) N-hydroxyphthalimide, 2.8 weight parts vanadomolybdophosphate ( $NPV_6Mo_6$ ) and 1,000 weight parts t-amyl alcohol was stirred for 5 hours at 100°C under an oxygen atmosphere. Upon investigating the product in the reaction solution, 44 weight parts benzophenone (24 % yield) were formed.

[0072] Practical Example 4

A solution mixture containing 184 weight parts (1 mole) benzhydrol, 11.3 weight parts (0.1 mole) N-hydroxyphthalimide and 1,000 weight parts benzonitrile was stirred for 5 hours at 100°C under an oxygen atmosphere. Upon investigating the product in the reaction solution, 36 weight parts benzophenone (20 % yield) were formed.

[0073] Practical Example 5

A solution mixture containing 108 weight parts (1 mole) benzhydrol, 16 weight parts (0.1 mole) N-hydroxyphthalimide and 1,000 weight parts benzonitrile was stirred for 10 hours at 100°C under an oxygen atmosphere. Upon investigating the product in the reaction solution, 66 weight parts benzaldehyde (23 % yield) were formed.

[0074] Practical Example 6

A solution mixture containing 108 weight parts (1 mole) benzhydrol, 16 weight parts (0.1 mole) N-hydroxyphthalimide, 2.8 weight parts vanadomolybdophosphate ( $NPV_6Mo_6$ ) and 1,000 weight

parts benzonitrile was stirred for 10 hours at 100°C under an oxygen atmosphere. Upon investigating the product in the reaction solution, 46 weight parts benzaldehyde (43 % yield) and 64 weight parts benzoic acid (52 % yield) were formed.

[0075] Practical Example 7

A solution mixture containing 168 weight parts (1 mole) diphenyl methane, 16 weight parts (0.1 mole) N-hydroxyphthalimide and 1,000 weight parts benzonitrile was stirred for 20 hours at 100°C under an oxygen atmosphere. Upon investigating the product in the reaction solution, 146 weight parts benzophenone (80 % yield) were formed.

[0076] Practical Example 8

A solution mixture containing 166 weight parts (1 mole) fluorene, 16 weight parts (0.1 mole) N-hydroxyphthalimide and 1,000 weight parts benzonitrile was stirred for 10 hours at 100°C under an oxygen atmosphere. Upon investigating the product in the reaction solution, 144 weight parts fluorenone (80 % yield) were formed.

[0077] Practical Example 9

A solution mixture containing 132 weight parts (1 mole) tetralin, 16 weight parts (0.1 mole) N-hydroxyphthalimide, 6.4 weight parts (0.025 mole) cobalt acetyl acetonate, and 1,000 weight parts benzonitrile was stirred for 10 hours at 100°C under an oxygen atmosphere. Upon investigating the product in the reaction solution, 144 weight parts fluorenone (80 % yield) were formed.

[0078] Practical Example 10

Except for not using cobalt acetyl acetonate and making the reaction time 5 hours, the carbon-hydrogen bond at the benzyl site was oxidized selectively upon doing the reaction in the same manner as in Practical Example 9, and 1-hydroxytetralin (13 % yield) and  $\alpha$ -tetralone (37 % yield) were formed.

[0079] Practical Example 11

Except for using 1 mole isochroman instead of 132 weight parts (1 mole) tetralin, isochroman-1-one (83 % yield) having a lactone ring was formed upon doing a reaction for 5 hours without using cobalt acetyl acetonate.

[0080] Practical Example 12

A solution mixture containing 136 weight parts (1 mole) adamantane, 16 weight parts (0.1 mole) N-hydroxypthalimide, 6.4 weight parts (0.025 mole) cobalt acetyl acetonate and 1,000 weight parts benzonitrile was stirred for 10 hours at 100°C under an oxygen atmosphere. Upon investigating the product in the reaction solution, 79 weight parts adamantanol (52 % yield) were formed.

[0081] Practical Example 13

A solution mixture containing 136 weight parts (1 mole) adamantane, 16 weight parts (0.1 mole) N-hydroxypthalimide and 1,000 weight parts benzonitrile was stirred for 10 hours at 100°C under an oxygen atmosphere. Upon investigating the product in the reaction solution, 36 weight parts adamantanol (24 % yield) were formed.

[0082]

Moreover, except for making the reaction time 5 hours, the reaction was done in the same manner as stated above and adamantanol was formed at a 12 % yield.

[0083] Practical Example 14

A solution mixture containing 84 weight parts (1 mole) cyclohexane, 16 weight parts (0.1 mole) N-hydroxyphthalimide and 1,000 weight parts benzonitrile was stirred for 10 hours at 100°C under an oxygen atmosphere. Upon investigating the product in the reaction solution, cyclohexanone was obtained at the standard 56 % inversion rate and 60 % selectivity for cyclohexane.

[0084]

In addition, at the 56 % inversion rate for cyclohexane and 89 % KA oil selectivity, cyclohexanone was obtained at a 36 % yield and cyclohexanol was obtained at a 4 % yield. Furthermore, 112 oxidized adipic acid was also obtained at a 10 % yield.

[0085] Practical Example 15

A solution mixture containing 84 weight parts (1 mole) cyclohexane, 16 weight parts (0.1 mole) N-hydroxyphthalimide, 6.4 weight parts (0.025 moles) acetyl acetonate and 1,000 weight parts benzonitrile was stirred for 10 hours at 100°C under an oxygen atmosphere. Upon investigating the product in the reaction solution, cyclohexanone was obtained at the standard 56 % inversion rate and 66 % selectivity for cyclohexane.

[0086]

In addition, at the 76 % inversion rate for cyclohexane and 88 % KA oil selectivity, cyclohexanone was obtained at a 28 % yield and cyclohexanol at a 2 % yield. Furthermore, oxidized adipic acid was also obtained at a 37 % yield.

[0087] Practical Example 16

As shown in Table 1, except for changing the amount of catalyst and the oxygen pressure, the reaction was done in the same manner as in Practical Example 15. Upon investigating the reaction product by gas chromatographic analysis, the results in Table 1 were obtained. Moreover, NHPI in the table denotes N-hydroxypthalimide and AA in Co(AA)<sub>3</sub> denotes acetyl acetone.

[0088]

[Table 1]

Table 1

Reaction Conditions			Reaction Products			
NHPI (mole %)	Co(AA) <sub>3</sub> (mole %)	Oxygen (atm)	Cyclohexane (Inversion Rate)	Cyclohexanone (Yield)	Cyclohexanol (Yield)	Adipic Acid (Yield)
10	2.5	10	76	28	2	37
20	2.5	10	82	28	2	42
10	10	10	79	28	2	39
10	2.5	30	96	23	1	47

Practical Example 17

As shown in Table 2, except for changing the type and amount of solvent as well as the reaction time, the reaction was done in the same manner as in Practical Example 15. Upon investigating the reaction product by gas chromatographic analysis, the results

in Table 2 were obtained.

[0089]

[Table 2]

Table 2

Reaction Conditions			Reaction Products			
NHPI (mole %)	Co(AA), (mole %)	Oxygen (atm)	Cyclohexane (Inversion Rate)	Cyclohexanone (Yield)	Cyclohexanol (Yield)	Adipic Acid (Yield)
Benzonitrile	1,000	6	76	28	2	37
Benzonitrile	600	6	93	25	1	39
Benzonitrile	1,000	15	91	26	1	45
Acetic Acid	1,000	6	86	14	2	47
Nitrobenzene	1,000	6	55	7	4	30
t-butanol	1,000	6	62	13	2	30

Practical Example 18

113

As shown in Table 3, except for changing the type and amount of the co-catalyst (cooxidant), the reaction was done in the same manner as in Practical Example 15. Upon investigating the reaction product by gas chromatographic analysis, the results in Table 3 were obtained. Moreover, NHPI denotes N-hydroxyphthalimide, AA denotes acetyl acetonate and OAc denotes an acetyl group.

[0090]

[Table 3]

Table 3

Reaction Conditions			Reaction Products			
NHPI (mole %)	Co(AA) <sub>2</sub> (mole %)	Oxygen (atm)	Cyclohexane (Inversion Rate)	Cyclohexanone (Yield)	Cyclohexanol (Yield)	Adipic Acid (Yield)
10	Co(AA) <sub>2</sub>	2.5	76	28	2	37
10	Co(AA) <sub>2</sub>	5	95	25	3	43
10	Co(AA) <sub>2</sub>	7.5	95	25	3	42
10	Ni(AA) <sub>2</sub>	2.5	39	8	9	14
10	Fe(AA) <sub>2</sub>	2.5	35	6	8	14
10	Ce(AA) <sub>2</sub>	2.5	74	30	2	34
10	SmCl <sub>3</sub>	2.5	40	15	6	10
10	RuCl <sub>3</sub>	2.5	61	20	3	25
10	CoCl <sub>2</sub>	2.5	80	23	2	40
10	Co(NO <sub>3</sub> ) <sub>2</sub>	2.5	86	21	2	43
10	Sm <sub>2</sub> O <sub>3</sub>	2.5	38	13	8	11
10	RuO <sub>2</sub>	2.5	66	5	4	39
10	Ce(OAc) <sub>3</sub>	2.5	49	18	4	20
10	CuCl <sub>2</sub>	2.5	96	23	1	47

Comparative Example 1

After stirring a solution mixture containing 184 weight parts (1 mole) benzhydrol and 1,000 weight parts benzonitrile for 5 hours at 100°C under an oxygen atmosphere and upon investigating the solution mixture by gas chromatographic analysis, the target oxidation product was not detected whatsoever.

[0091] Comparative Example 2

After stirring a solution mixture containing 184 weight parts (1 mole) benzhydrol, 2.8 weight parts vanadomolybdophosphate and 1,000 weight parts benzonitrile for 5 hours at 100°C under an oxygen atmosphere and upon investigating the solution mixture by gas chromatographic analysis, the target oxidation product was not detected whatsoever even though a partial loss of the raw material constituents was confirmed.

[0092] Comparative Example 3

After stirring a solution mixture containing 184 weight parts (1 mole) benzhydrol, 6.4 weight parts (0.025 mole) cobalt acetyl acetonate and 1,000 weight parts benzonitrile for 5 hours at 100°C under an oxygen atmosphere and upon investigating the solution mixture by gas chromatographic analysis, the target oxidation product was not detected whatsoever even though a partial loss of the raw material constituents was confirmed.